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Ecofriendly production of ethylene by dehydration of ethanol over $Ag_3PW_{12}O_{40}$ salt in nitrogen and air atmospheres

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ABSTRACT

Neutral silver salt of tungstophosphoric acid $Ag_3PW_{12}O_{40}\cdot 3H_2O$ (AgPW) was investigated as the catalyst in the gas-phase dehydration of ethanol, in the temperature range of 373–493 K. The relative humidity of atmosphere (nitrogen or air) was changed from 2% to 10%. It was shown that relative humidity of both atmospheres strongly influences the catalytic activity of AgPW salt. The thermal stability of AgPW salt was determined with simultaneous DSC/TG analysis and high temperature XRD method. It was demonstrated that one molecule of water, which hydrates silver cation loses the salt structure in the temperature range of 473–523 K. The stability of primary and secondary structure of AgPW salt after reaction was investigated using FT-IR and XRD techniques. The AgPW salt is stable, when relative humidity attains at least 10% independent of atmosphere in which reaction is performed. In such conditions and at 473 K the AgPW catalyst exhibited the conversion of ethanol as well as the selectivity to ethylene about 99%. It can be concluded that $Ag_3PW_{12}O_{40}\cdot 3H_2O$ salt can be used as an 'ecofriendly' catalyst for ethylene production by the dehydration of ethanol in nitrogen or air atmospheres in relatively low temperature and appropriate relative humidity.

1. Introduction

Ethylene is one of major starting material for petrochemical industry, which is used in the preparation of many products, e.g. polyethylene, ethylene oxide, ethylene dichloride or ethylbenzene. Alkenes can be produced by cracking of higher hydrocarbons but this process is energy consuming because it operates at very high temperatures above 1123 K. Moreover, under these conditions the yield of the process is about 55% only. Oxidative dehydrogenation of ethane has been reported as an alternative method, which allows for obtaining ethylene at lower temperatures [1,2]. Unfortunately, this process forms many side products because of the presence of oxygen. Selective oxidation of ethanol can be also used as a route to produce ethylene as well as acetaldehyde; however, the mesoporous vanadium-incorporated MCM-41 used as a catalyst is rapidly deactivated [3]. Thus, the production of ethylene by catalytic dehydration of ethanol seems to be important and alternative route since ethanol can be easily obtained from renewable sources like biomass. On the other hand, diethyl ether, which can be also produced by the dehydration of ethanol, has very attractive fuel properties because of high cetane number of 85–96.

In the recent years, catalytic dehydration of ethanol to ethylene was investigated using transition metal oxide [4], zeolite [5–9], silica–alumina [9] or heteropolyacid, pure [10] or impregnated on MCM-41 and silica [11,12]. Among them, the heteropolyacids and their salts seem to be promising catalysts in improving the yield of ethylene as well as lowering the temperature of reaction compared to γ-alumina. The main problem of catalytic dehydration of ethanol to ethylene is side reaction leading to acetaldehyde at both lower [12,13] and higher temperatures [5,7]. The catalytic behaviour of metal salts of heteropolyacids attracts considerable interest because the formation of salts may lead to the appearance of a bifunctional or multifunctional catalysis [14]. Most of the reactions were proceeded both on the acidic form of heteropoly compound and on the neutral salts, even in the case of the reactions catalyzed by acids [15].

High catalytic performance of neutral silver salt $Ag_3PW_{12}O_{40}$ is well known in both homogeneous and heterogeneous reactions [16–22]. This salt is characterized by outstanding acidity, which measured, e.g. by ammonia sorption is about one order of magnitude higher than neutral cesium salt $Cs_3PW_{12}O_{40}$ [23]. It can be caused by the presence of water coordinating silver cations in AgPW structure [24], which is different than the structure of neutral cesium or potassium salts of tungstophosphoric acid. Niiyama et al. [25] suggested that water coordinated to the metal cation generates protons according to the following reaction:

$$M^{n+} + mH_2O \rightarrow [M(H_2O)_m]^{n+} \rightarrow [M(H_2O)_{m-1}(OH)]^{(n-1)+} + H^+$$

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Recently, it was shown that protons generated by dissociation of water coordinated to the silver atoms can influence the catalytic activity of AgPW salt [26].

In this work we report the catalytic activity of neutral silver salt of tungstophosphoric acid in the ethanol dehydration carried out in two different atmospheres, nitrogen and air, with different relative humidity. The aim of presented work was to show that at lower temperature the main factor influencing catalytic activity of AgPW salt is relative humidity of atmosphere, in which reaction is performed. In order to study the thermal stability of the $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ structure the DSC/TG and high temperature XRD methods were applied. The stability of primary and secondary structure of AgPW salt after reaction was investigated using FT-IR and XRD techniques.

2. Experimental

2.1. Catalyst preparation

The silver salt $Ag_3PW_{12}O_{40}$ (denoted in the text as AgPW) was obtained by mixing a commercially available 12-tungstophosphoric acid ($H_3PW_{12}O_{40}{\cdot}24H_2O$, HPW, Sigma–Aldrich) with silver nitrate ($AgNO_3$, p.p.a., POCh) as the source of silver ions. In the standard procedure 15 mL of $AgNO_3$ aqueous solution (0.4 M) was introduced to 20 mL of HPW aqueous solution (0.1 M). The preparation process was performed at ambient temperature without stirring. The obtained mixture was evaporated overnight in the oven at 353 K to dryness.

2.2. Catalytic tests

The catalytic experiments were carried out in a conventional flow-type reactor under atmospheric pressure in the temperature range of 373–493 K. As a carrier gas the nitrogen or air of various relative humidity (RH), i.e. 2 or 10% was used (denoted in the text as nitrogen-2%, air-2% or nitrogen-10%, air-10%, respectively). The synthetic air-2% was obtained from nitrogen and oxygen compressed in the cylinders (Linde Gaz Polska), both with ca. 2% of relative humidity. The RH of air-10% and of nitrogen-10% was obtained by mixing the air-2% or nitrogen-2% with water vapour. The relative humidity of flowing gas was measured at 293 K using hygrometer PWT-411 (ELMETRON). Typically, a 0.5 cm^3 of sample (0.25–0.50 mm mesh) was packed into quartz reactor and stabilized in the flowing gas for 1 h. The ethanol was introduced into applied atmosphere by an evaporator–saturator set placed in a thermostat. The concentration of ethanol was about 15 $g\,m^{-3}$, whereas GHSV was equal to 6000 h^{-1}. The reaction was performed until the conversion of ethanol and the products distribution was stable. Usually, it took about 0.5–1.0 h. Next, the catalyst was heated at a rate of 2 K/min to the higher reaction temperature and the procedure was repeated consecutively. All the tests were performed at the same temperature and time scheme. The reaction products were analysed using SRI 8610B gas chromatograph equipped with HayeSep D packed column (3 m, 100–120 mesh) and both TCD and FID detectors arranged one by one. Thus, with one sample injection all products were detected and recognized. The amounts of products were calculated from calibration curves prepared for each measured compound.

2.3. Catalysts characterization

The specific surface areas of the AgPW samples were determined using the BET method. Prior to the measurements, the samples were heated and degassed under vacuum at 473 K for 2 h. The adsorption–desorption isotherm for nitrogen was obtained at 77 K using an Autosorb-1, Quantachrome equipment. The isotherm for water vapour was obtained at 297 K with Hydrosorb 1000 (Quantachrome).

The FT-IR spectra were recorded using Nicolet 380 FT-IR spectrometer with standard KBr pellets technique. Prior to measurements, the samples were dried at 393 K in order to remove crystallization water. The measurements were performed for the salt 'as synthesized' and for the samples after dehydration of ethanol performed in nitrogen and air of different relative humidity.

The simultaneous DSC/TG measurements were performed in the flow of nitrogen-2%, air-2% and air-10% (30 ml/min) using Netzsch STA 409 PC Luxx apparatus. In all cases the samples of about 40 mg were heated in the range of 293–600 K with the heating rate of 10 K/min.

The X-ray diffraction patterns were collected using the Siemens D5005 diffractometer equipped with the Anton Paar XRK900 reaction chamber and the graphite monochromator of the diffracted beam. The CuKα radiation (40 kV, 30 mA) was used. The patterns of 'as synthesized' AgPW salt at 293 K and of samples annealed at 473, 498, 523, 548 and 573 K were recorded in the 2θ range of 8–65°, of step size = 0.02°, 1 s/step. Before each XRD measurement the sample was stabilized for 1 h in respective temperature.

The microcalorimetric measurements of ammonia sorption were carried out at 293 K using MICROSCAL gas flow-through microcalorimeter [27]. Prior to the experiments the samples were preheated at 473 K for 2 h in the flow of helium within the microcalorimetric cell. After cooling down and equilibrating the system thermally at 293 K ammonia was adsorbed from the helium carrier gas containing 1% of NH_3 flowing through the cell at 1 cm^3/min under normal pressure. Concurrently with the heat evolution, the uptake of ammonia from the carrier gas was measured using thermoconductivity detector (downstream detector, DSD).

2.4. Stability of AgPW structure during reaction

The investigations of AgPW structure stability after reaction were carried out using FT-IR spectroscopy and XRD method. The measurements were performed for all samples obtained after reaction in nitrogen and in air with various relative humidity. Additionally, the adsorption–desorption isotherms were obtained for the used catalysts.

3. Results and discussion

3.1. Catalyst preparation

The pH of the $H_3PW_{12}O_{40}$ solution during precipitation of its salt is a fundamental factor influencing the formation of various heteropolyacid structures, other than the Keggin structure, e.g. lacunary anions, which may affect the surface area of the obtained samples [28]. In the present work, in order to prevent decomposition of Keggin anion in tungstophosphoric acid the precipitation of AgPW salt was always performed at the pH 1. To confirm its composition the elementary analysis was performed using the ICP (Inductively Coupled Plasma) method, which showed the Ag/Keggin anion ratio equal to 3.04. It is in a good agreement with the stoichiometric composition of $Ag_3PW_{12}O_{40}$ salt and corroborates the total substitution of protons by silver cations. Thus, the influence of residual protons existing in the salt structure on catalytic activity of studied catalyst can be potentially excluded.

Several authors have previously postulated the existing of residual protons in the structure of heteropolysalts obtained by the substitution of, e.g. cations in the $(NH_4)_3PW_{12}O_{40}$ by other monovalent cations like K^+ or Cs^+ [29,30]. Alike, Parent and Moffat [31,23] considered the presence of residual protons in neutral

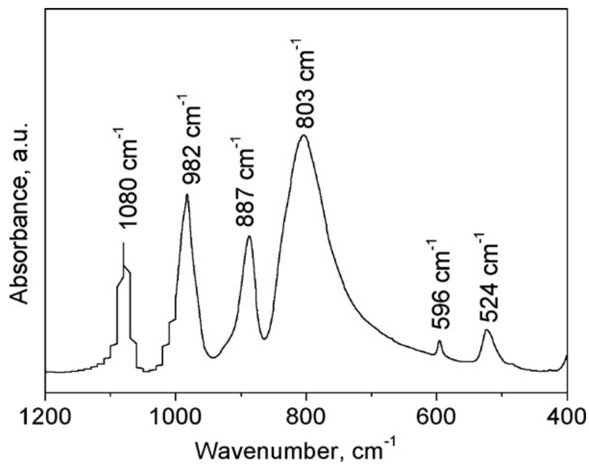

Fig. 1. The FT-IR spectrum of AgPW salt.

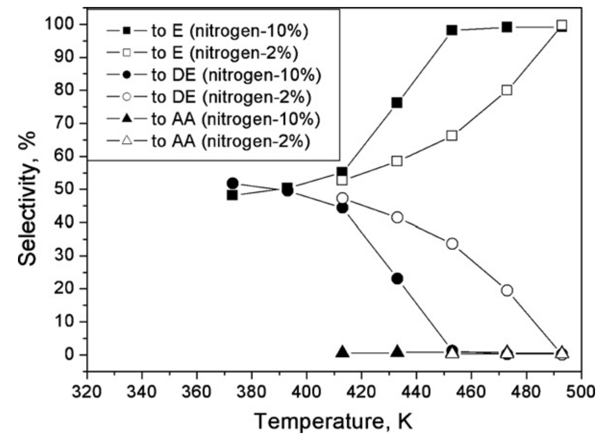

Fig. 3. Selectivity to products in dehydration of ethanol performed in nitrogen-2% and nitrogen-10% on AgPW salt (where, E = ethylene, DE = diethyl ether, AA = acetaldehyde).

silver salts $Ag_3PW_{12}O_{40}$. However, in these papers the presence of water molecules hydrating silver cations in the structure of AgPW salt was not taken under account. Recently, the structure of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt was determined in our paper [24]. It was also showed previously that the presence of these water molecules strongly influences its, e.g. catalytic activity [26].

The primary structure of the AgPW salt was investigated using FT-IR spectroscopy. Fig. 1 shows the FT-IR spectrum of 'as synthesized' AgPW salt obtained in the 'fingerprint' region of Keggin anion. The characteristic bands were observed at 1080, 982, 887 and 803 cm^{-1}. They can be assigned to the stretching vibrations of P—O_i, W═O_t, W—O_c—O and W—O_e—W occurring within Keggin anions, respectively [32]. The bands at 596 and 524 cm^{-1} can be ascribed to bending vibrations of O_i—P—O_i and W—O_e—W, respectively. It should be stressed that no bands originating from others form of heteropoly compounds were recorded. Thus, it can be concluded that prepared AgPW salt used in catalytic tests was composed of Keggin anions, only. This is very important for applications of neutral silver salt of HPW and clarity of conclusions.

The acidity of AgPW salt was tested in microcalorimetric measurements of ammonia sorption and was compared with that obtained for bulk HPW. It was observed that the tungstophosphoric acid and its neutral silver salt sorbed ammonia irreversibly and the uptake of ammonia referred to 1 mol of acid or salt is higher than one. Irreversible uptake of ammonia on heteropolyacid attained 1.3 mol NH_3/mol whereas in case of AgPW salt about 3.9 mol NH_3/mol only. The saturation of HPW with ammonia is far from the equilibrium, in which at least 3 moles of ammonia per 1 mole of HPW could be expected. It can be suggested that ammonia penetrates partially the bulk of heteropolyacid. In turn, the sorption of ammonia on AgPW salt is connected with the presence of water molecules hydrating silver cations according to the mechanism of protons generation proposed by Niiyama et al. [25]. Thus, these results show that residual protons, if exist in AgPW salt, cannot significantly influence its acidity as well as its catalytic activity.

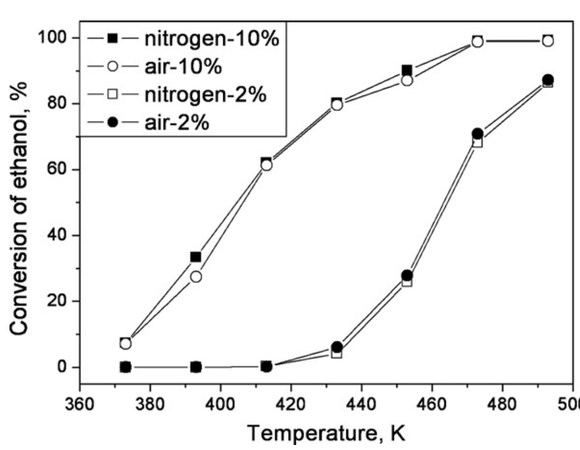

Fig. 2. Ethanol conversion obtained on AgPW salt in nitrogen and in air with various relative humidity.

The irreversible molar heat was 90.8 kJ/mol NH_3 for AgPW salt and 139.9 kJ/mol NH_3 for HPW. The first value is close to 99.0 kJ/mol NH_3, which is assigned to the formation of $[N_2H_7]^+$ adducts [33,34], while the second value to the formation NH_4^+ cations [35]. It indicates that $[N_2H_7]^+$ adducts are easier formed on AgPW salt compared to HPW, what is important from catalytic point of view. It seems that $[C_2H_5OH]_2H^+$ adducts, which lead to diethyl ether, should be also easier formed on AgPW sample.

3.2. Catalytic tests

The investigations of catalytic activity of AgPW salt were performed using dehydration of ethanol in the temperature range of 373–493 K in nitrogen and in air atmospheres with different relative humidity of 2% and of 10%. This reaction is often used as the test reaction to compare the catalytic activity of acidic catalysts because involves protons. As it is seen in Fig. 2 the profiles of ethanol conversions obtained in both nitrogen-2% and air-2% are similar as well as those obtained in nitrogen-10% and air-10%. However, the significant difference in catalytic activity of AgPW salt appears, when the relative humidity of both atmospheres is changed from 2% to 10%. It clearly shows that not atmosphere but its relative humidity plays very important role in dehydration of ethanol.

Usually, the dehydration of ethanol is performed in neutral atmospheres like nitrogen or helium [4–12] and leads to such products as ethylene, diethyl ether and acetaldehyde. These compounds were also found in our reaction products. However, application of air as reaction atmosphere caused that traces of some products resulted from the presence of oxygen, like acetic acid and ethyl acetate, appeared. Their summary amount did not exceed 0.1% independently of relative humidity of air. It should be mentioned that also traces of carbon dioxide was recorded. The concentration of carbon dioxide was amounted to 0.04% close to its value in air, in which the reaction was performed.

Figs. 3 and 4 show that also the selectivity to products depends on RH of atmosphere, in which the reaction is performed. The selectivity to ethylene grows while the selectivity to diethyl ether diminishes with increasing temperature in the both atmospheres,

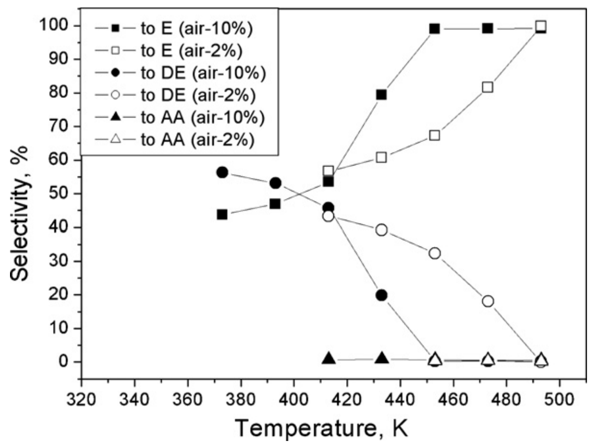

Fig. 4. Selectivity to products in dehydration of ethanol performed in air-2% and air-10% on AgPW salt (where, E = ethylene, DE = diethyl ether, AA = acetaldehyde).

independently of relative humidity. However, in nitrogen-10% and in air-10% the selectivity to ethylene attains about 99.0% already at 453 K and then practically remains unchanged up to 493 K whereas in nitrogen-2% and in air-2% reaches about 67% at 453 K and finally about 99% at 493 K. The selectivity to acetaldehyde did not exceed 0.7% in both atmospheres.

Comparing the selectivities to ethylene, diethyl ether and acetaldehyde obtained in nitrogen-2% and air-2% (Figs. 3 and 4) it can be observed that they are similar as well as those in nitrogen-10% and air-10% (Figs. 3 and 4). Thus, it can be concluded that the dependence of selectivity to products from RH of both atmospheres turned out to be the same as in case of conversions of ethanol.

These observations can be compared to some extent with results presented in the literature, in which the use of HPW or its salt as the catalysts in dehydration of ethanol was also described. The pure tungstophosphoric acid was investigated in the temperature range of 413–523 K and showed the highest yield to ethylene of over 75% at 523 K [10]. However, the presence of water in the feed stream caused some decrease of its catalytic activity. It was suggested that water (10% water in ethanol) is adsorbed more strongly than ethanol on catalyst surface causing reduction of available active sites for ethanol. Silver salts of HPW supported on silica were also investigated in discussed reaction [12]. The highest conversion of ethanol of about 99% was obtained using $Ag_2HPW_{12}O_{40}$ salt supported on silica at 448 K. Also catalyst consisting of 30% of HPW supported on montmorillonite K-10 was applied in dehydration of dilute bio-ethanol (80% m/m) [36]. It was found out that ethanol conversion of 74% and selectivity to ethylene of 92% was reached at 523 K. In all presented experiments helium or nitrogen was used as the carrier gas for ethanol. It can be supposed that the relative humidity of carrier gases was very low and similar to other gases compressed in the cylinders as nitrogen used in our experiments. However, different applied space velocities make the direct comparison of catalytic activity as well as selectivity to ethylene difficult. On the other hand, the experiments with the presence of water vapour in flowing gas [36] showed its influence on catalytic activity of investigated catalysts, which confirms our observations.

It was reported earlier that the dehydration of ethanol is not particularly sensitive to the strength of the acid sites whereas strongly depends on their concentration [37]. Thus, the presence of water hydrating silver cations in AgPW salt play very important role in generation of protons needed to an acidic type reaction according to the observation of Niiyama et al. [25]. It can be also suggested that much higher catalytic activity of AgPW catalyst in nitrogen-10% and air-10% resulted from the stability of its hydrated structure compare to that existing in atmosphere with 2% of relative humidity. However, it was earlier showed that such catalyst preheated to 493 K during reaction in air with 2% of RH can easy recover its secondary structure after exposition to air with high relative humidity [26]. Similar behaviour was observed in case of $H_3PW_{12}O_{40}{\cdot}6H_2O$ structure, which is stable to 448 K and then starts to lose water coordinating protons. This process is finished at 503 K [38]. It seems that the dehydration process of HPW and its neutral silver salt AgPW demonstrates high sensitivity to relative humidity of surrounding atmosphere.

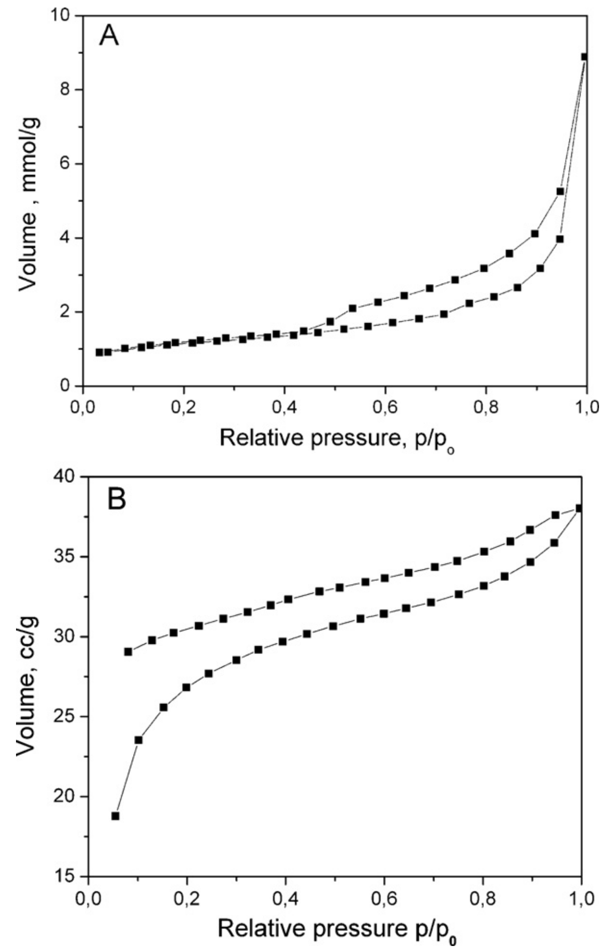

Fig. 5. Nitrogen (A) and water vapour (B) adsorption–desorption isotherms for AgPW salt.

In order to explain why catalytic activity of AgPW catalyst depends on relative humidity of atmosphere, in which dehydration of ethanol is performed, the characterization of AgPW salt was carried out by means of BET, FT-IR, XRD and simultaneous DSC/TG techniques.

The nitrogen adsorption–desorption isotherm obtained for AgPW salt was found to be reversible and classified as type IIb with hysteresis loop of H3 type (Fig. 5A), what indicates for the presence of slit shaped pores. The calculated BET specific surface area was equal to 4.0 m^2/g. However, this was not the case when the isotherm of water vapour was applied for the same purpose (Fig. 5B). The specific surface area calculated from the water vapour isotherm was drastically different and attained 70.1 m^2/g. This difference can be partially explained by various kinetic diameters of water (0.265 nm) [39] and of nitrogen (0.364 nm) [40,41] molecules, what is crucial for their penetration inside the microporous structure. However, other properties of molecules like polarity may also influence this effect. The similar

effect was described previously in our paper concerning cesium salt of tungstophosphoric acid $Cs_2HPW_{12}O_{40}$ prepared from different reagents [42]. It turn out that $Cs_2HPW_{12}O_{40}$ prepared from cesium carbonate had specific surface area calculated from nitrogen adsorption–desorption isotherm equal to 1 m^2/g whereas calculated from water vapour adsorption–desorption isotherm was 89.5 m^2/g. The same salt prepared using cesium chloride had specific surface area calculated from nitrogen and water vapour equal to 78.2 and 85.7 m^2/g, respectively. It was clearly showed that the isotherm of water vapour can be used to determine the specific surface area similarly to isotherm of nitrogen. Thus, it can be concluded that nitrogen molecules does not penetrate the bulk of AgPW salt in contrast to water molecules, which can be easy sorbed. The specific surface area measured with nitrogen molecules can be ascribed to external surface area of AgPW salt while the specific surface area measured with water molecule involves both external and internal surface areas. As was described earlier the sorption of molecules with various sizes is often used to determine the diameter of ultramicropores in such materials as heteropolysalts [43].

It also shows how crucial role can play the water molecules when the dehydration of ethanol is performed in atmosphere with different relative humidity. It was earlier demonstrated that kind of anion [42,44] and kind of cation [45] in the precipitating agent can influence the specific surface area, pore volume and pore width of heteropolysalts. Thus, it can be concluded that apart from kind of anion and cation in the precipitating agent also water hydrating cation in heteropolysalts can influence their catalytic activity.

One can speculate that the amount of water arising as the product of dehydration of ethanol is sufficient to stabilize the $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ structure and simultaneously is the source of protons [25]. However, the results presented in our previous paper concerning dehydration of ethanol on $Ag_3PMo_{12}O_{40}{\cdot}3H_2O$ salt [26] clearly showed that the water originating from reaction as well as higher relative humidity of atmosphere were insufficient to stabilize its structure. This was related to lower thermal stability of AgPMo structure in comparison to AgPW salt.

The influence of rising temperature on AgPW structure in nitrogen-2% and air-2% was investigated using DSC/TG method. The results of measurement performed in nitrogen-2% are shown in Fig. 6A while those obtained in air-2% in Fig. 6B. The lower relative humidity of both atmospheres was chosen to facilitate the removal of water. Both DSC curves demonstrate several endothermic effects connected with the loss of water. The first two minima appearing at 363–366 K and 423 K are characteristic for the removal of physisorbed and crystallization water molecules, respectively. The endothermic effects, which appeared between 433 and 585 K are connected with the loss of water hydrating silver cations. It can be suggested that the minimum at 479 K is related to the loss of water in the sub-surface region of AgPW salt whereas that at 539 K with the removal of water from the bulk. This also shows that the surface of AgPW salt is more sensitive on temperature than the bulk.

Taking into account the TG measurements, it can be possible to determine the mass loss connected with described process. This value attains 1.57 wt% in both atmospheres what corresponds to 2.84 molecules of the water and shows that $[Ag(H_2O)]^+$ complex exists in the AgPW structure up to about 433 K. Its presence and location in the centre of octahedral space between the Keggin anions was described in our previous paper [24]. Similar DSC/TG results obtained for the measurements performed in nitrogen-2% and in air-2% strongly indicate that the kind of atmosphere flowing by the AgPW samples does not influence their thermal stability. Both DSC measurements were performed to 600 K and showed no effects, which could be interpreted as the AgPW salt decomposition. This is in a good agreement with the results obtained by Haber et al. [12,13], which found out that AgPW salt is stable up to at least 890 K. Thus, it can be summarized that in atmosphere with 2% of relative humidity and in the temperature range of catalytic tests, AgPW salt preserves its structure consisting of Keggin anions. However, the silver cations, which are hydrated by water up to 433 K at higher temperatures starts to lose this water. It can be suggested that this process can strongly influence catalytic activity of AgPW salt.

On the other hand, the total amount of water in AgPW salt measured in both atmospheres with 2% of relative humidity was about 2.25 wt% (Fig. 6). Taking into account that AgPW salt readily absorbs water molecules (Fig. 5B) the influence of RH of air on total content of water was studied. Therefore, additional TG measurement was performed in air-10%. Obtained result was compared with that in air-2% (Fig. 6B) and is presented in Fig. 7.

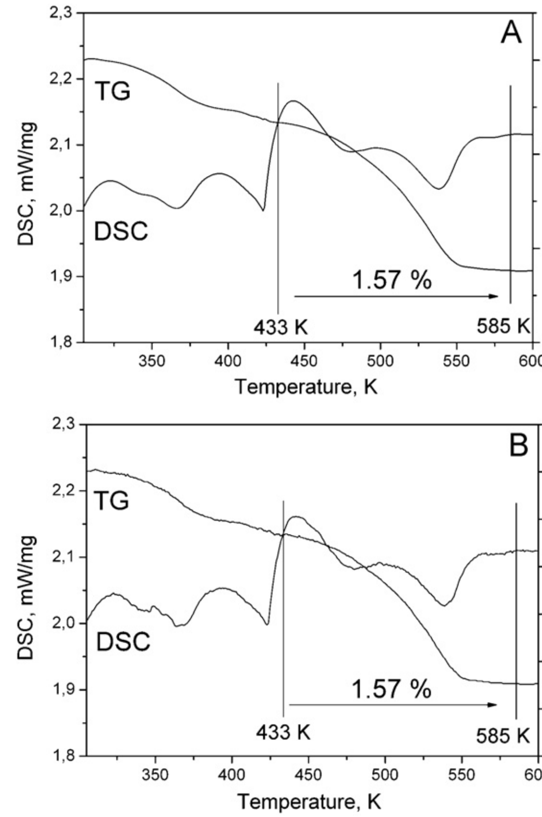

Fig. 6. DSC/TG measurements of AgPW performed in nitrogen-2% (A) and in air-2% (B).

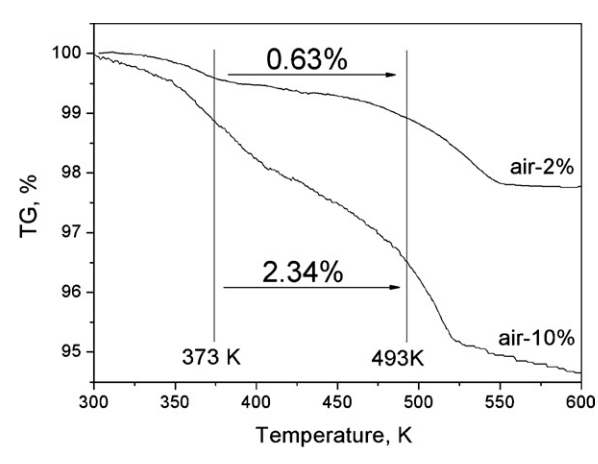

Fig. 7. Loss of water from AgPW structure obtained in air-2% and air-10% in the temperature range of ethanol dehydration.

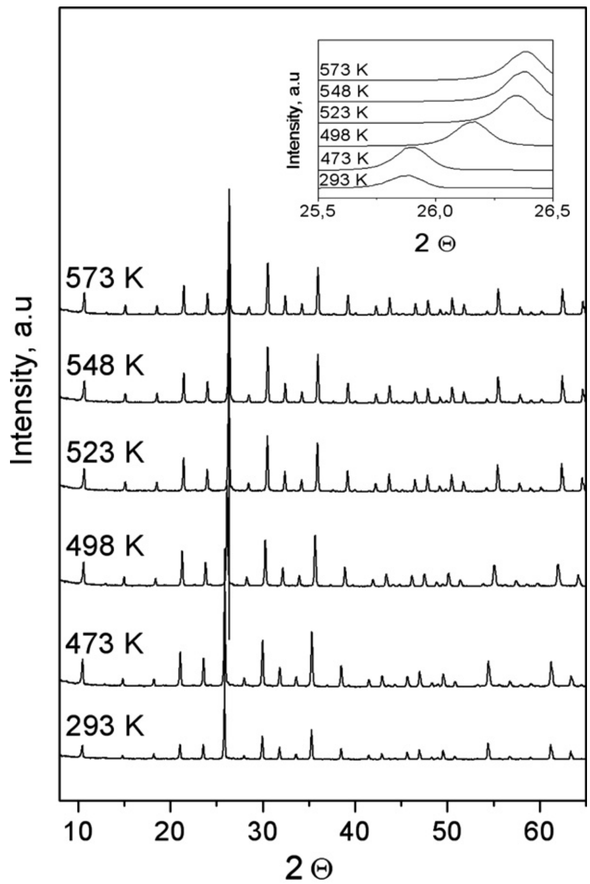

Fig. 8. XRD patterns obtained for AgPW salt annealed for 1 h at different temperatures in air-25%.

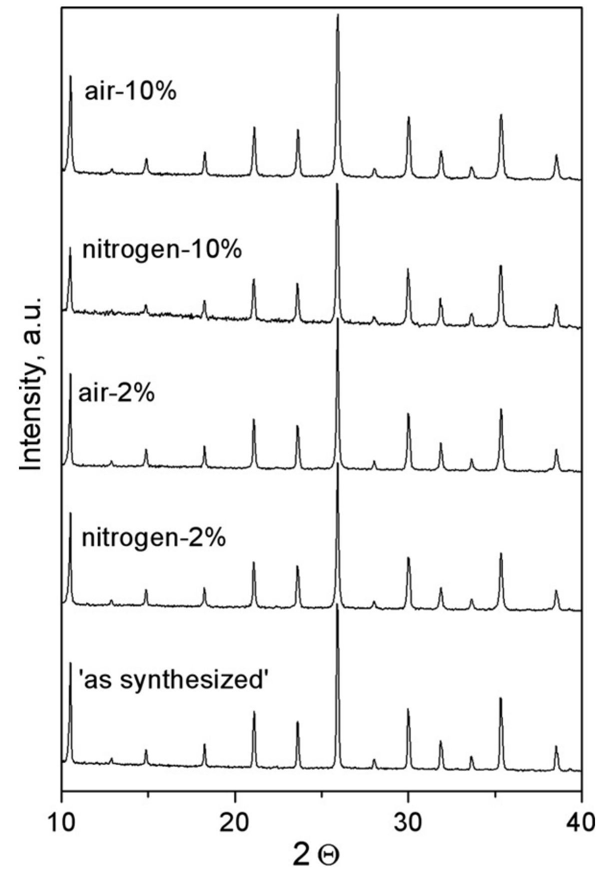

Fig. 9. XRD patterns obtained at 293 K for AgPW salt 'as synthesised' and after reaction in nitrogen and air with different relative humidity.

The TG curves show the difference in total amount of absorbed water in air with various relative humidity, which is equal to 2.25 wt% in air-2% and 5.36 wt% in air-10%. However, from catalytic point of view the difference in amount of absorbed water in the temperature range of reaction (373–493 K) is most interesting. As it is seen in Fig. 7 this value changed significantly from 0.63 wt% in air-2% to 2.34 wt% in air-10%. Thus, the consumption of water by AgPW salt can be the main reason influencing its catalytic activity in both applied atmospheres because water play important role in protons generation. This conclusion is in line with results obtained previously using XPS spectroscopy [26].

In order to check out the thermal stability of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ structure the high temperature XRD measurements were performed in the temperature range of 293–573 K in air with relative humidity of 25% (air-25%). The XRD patterns of AgPW salt annealed for 1 h at 473, 498, 523, 548 and 573 K were recorded in the range of 8–65° of 2θ and compared with XRD pattern obtained at 293 K (Fig. 8).

All XRD patterns of AgPW salt (Fig. 8) show the presence of one phase only and the reflections close to those of the cubic structure of $H_3PW_{12}O_{40}{\cdot}6H_2O$ [46]. No reflections originating from any other crystal phases are observed. The patterns of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ structure obtained at 293 and at 473 K (Fig. 8) are very similar with the lattice parameter estimated to 1.193 nm. The lattice parameter for the sample annealed at 498 K is shortened to 1.180 nm while that for sample annealed at 523 K is stabilized to 1.168 nm. As the example the shift of the (2 2 2) reflection at 25.88° of 2θ existing at 473 K to 26.40° of 2θ at 523 K is shown also in Fig. 8. It indicates the removal of the water hydrating silver cations between 473 and 523 K as well as the change of secondary structure of AgPW salt. Alike, the shortening of lattice parameter during the loss of water solvating protons was also observed when the structure of $H_3PW_{12}O_{40}{\cdot}6H_2O$ with a = 1.215 nm [46] changed into $H_3PW_{12}O_{40}{\cdot}3H_2O$ structure with a = 1.176 nm in the temperature range of 413–453 K [47].

The high temperature XRD results show that the loss of water hydrating silver cations in AgPW structure starts at 473 K in air-25%. This is in contrast to result obtained in DSC/TG – experiment performed in air-2%, when this value attained 433 K only (Fig. 6). It clearly indicates that the relative humidity of atmosphere influences strongly the temperature, at which the water hydrating silver cations starts to release.

However, it was shown previously [26] that AgPW salt annealed at 573 K can easy restore its structure after cooling to 293 K in atmosphere with higher relative humidity. It indicates for flexibility of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ structure what can facilitate its restoring.

3.3. Stability of AgPW structure during reaction

From application point of view, apart from high catalytic activity, the stability of a catalyst during reaction is also very important. Therefore, the investigations of stability of the Keggin anion existing in the structure of AgPW salt during reaction in both used atmospheres were carried out with FT-IR and XRD methods. The results are presented in Table 1 and in Fig. 9. As it is seen in Table 1, the set of characteristic bands obtained for AgPW salt remains unchanged independently of relative humidity of atmosphere, in which reaction was performed. The relative ratio of bands intensities did not change significantly what indicates that the Keggin anions in AgPW structure remain stable during the reaction in nitrogen or air with different relative humidity. Similarly, the small band at 1615 cm^{-1} as well as the broad bands at 3466 and

Table 1
The comparison of vibration bands obtained for AgPW salt in nitrogen and air with different relative humidity after reaction up to 493 K.

AgPW catalyst	Stretching vibrations (cm^{-1})				Non-protonated water	OH groups	
	P—O$_i$	W═O$_t$	W—O$_c$—W	W—O$_e$—W			
'as synthesised'	1080	982	887	803	1615	3466	3518
in nitrogen-10%	1080	982	887	802	1617	3469	3516
in nitrogen-2%	1080	982	888	801	1620	3470	3513
in air-10%	1079	981	887	800	1616	3469	3517
in air-2%	1079	984	889	801	1618	3468	3513

3518 cm^{-1}, which lie in the region where the O—H vibrations are usually observed [48], did not changed their positions within accuracy of the instrument. It means that the primary structure of AgPW salt stay unchanged after dehydration reaction performed in air with various relative humidity. However, it is possible that the samples of AgPW obtained after reaction in lower relative humidity have been hydrated again in laboratory atmosphere i.e. air-25%.

The origin of the small band of 1615 cm^{-1} is still unclear. In case of heteropolyacids and their acidic salts the band at 1615 cm^{-1} is often attributed to the vibration of protonated water located in the secondary structure [49,50]. In contrast, other authors assigned the band at 1700–1710 cm^{-1} to protonated water [51]. Paze et al. [52] have postulated that fully hydrated tungstophosphoric acid is characterized by a broad asymmetric band at 3510 cm^{-1} associated with both neutral and protonated water species and by two bands at 1720 and 1620 cm^{-1}, respectively. The bands at 3510 and 1620 cm^{-1} are mainly due to neutral water in the outer solvation sphere, while the band at 1720 cm^{-1} is assigned to H_3O^+ groups. In case of tungstosilicic acid, Bielanski et al. [53] observed that after evacuation of water at room temperature, the band at 1616 cm^{-1} vanished. This effect is due to the loss of loosely bonded water. It was also confirmed in case of potassium salts of tungstophosphoric acid [54]. When the number of hydrated protons in heteropolyacid decreases because of substitution by potassium cations, the intensity of the band at 1720 cm^{-1} progressively decreases, while intensity of the band at 1620 cm^{-1} increases [47]. In neutral silver salt AgPW described in the present paper the silver cations, which replaced acidic protons in heteropolyacids, are also hydrated by water [24]. Thus, the existing band at 1615 cm^{-1} can be assign to vibration of non-protonated water as well as to vibration of water hydrating silver cations.

The broad bands appearing at 3466 and 3518 cm^{-1} can be assigned to the stretching vibrations of OH groups. Bielanski et al. [55] investigated the dehydration of $H_3PMo_{12}O_{40}$ acid with FT-IR spectroscopy and reported that the loss of water molecules was accompanied by vanishing of the 3560 cm^{-1} band. Similar phenomenon was also observed in case of tungstosilicic acid [53]. It was suggested that the band observed at 3445 cm^{-1} is characteristic for protonated water, whereas that at 3550 cm^{-1} can be ascribed to loosely bonded water molecules. In case of AgPW samples the band at 3513–3518 cm^{-1} can be assigned to loosely bonded water while that at 3466–3470 cm^{-1} to water hydrated silver cations. The intensity of the band related to loosely bonded water showed only slight decrease after reaction in atmosphere with lower value of RH in contrast to the band belonging to $[Ag(H_2O)]^+$ complex. This means that the secondary structure of the AgPW salt was stable independently of the relative humidity of atmosphere or easily can be restored in atmosphere with higher relative humidity.

To confirm this conclusion the investigations of structure stability of AgPW salt after reaction were also performed by means of X-ray diffraction method. In order to demonstrate the changes in the salt structure the patterns obtained for the samples after reaction in air-2%, air-10%, nitrogen-2% and nitrogen-10% in the range of 10–40° of 2θ are shown in Fig. 9. The patterns of all AgPW samples are very similar and exhibit one phase only. No reflections originating from any other phases are observed. The lattice parameter of AgPW structure at 293 K was estimated to 1.193 nm, which is characteristic for $Ag_3PW_{12}O_{40}\cdot 3H_2O$ salt [24]. The same lattice parameter was calculated for the all samples obtained after reaction in different relative humidity, which were cooled to ambient temperature in air-25%. It indicates that the AgPW salt is stable in reaction conditions independently of relative humidity of atmosphere or easy recovers its hydrated structure due to exposure of the samples before measurements on surrounding atmosphere containing water vapour. This observation is consistent with FT-IR results presented in Table 1, which also showed the stability of AgPW salt after dehydration of ethanol.

In order to check out the influence of relative humidity of air applied in catalytic experiments as well as the reaction temperature on textural properties of AgPW salt the adsorption–desorption isotherms were obtained for both used catalysts (Fig. 10). Both isotherms represent mesoporous structure of studied catalyst. The experiments clearly show that catalytic conditions did not change the character of the isotherm of 'as received' AgPW salt. As it is seen, the isotherm obtained after reaction in air-10% (Fig. 10A) did not changed significantly compare to that before reaction (Fig. 5A). More changes are observed in the isotherm obtained after reaction in air-2% (Fig. 10B). The sample after dehydration of ethanol in air-10% was characterized by the specific surface area of 3.1 m^2/g and pore diameter of 3.8 nm. These values are similar to those obtained for 'as received' sample, 4.0 m^2/g and 4.2 nm, respectively. The AgPW salt after reaction in air-2% had pores with 2.7 and 5.4 nm of diameter while its specific surface area was equal to 1.0 m^2/g. This shows that in atmosphere with lower relative humidity the tertiary structure of AgPW salt easier formed a new porosity consisting of new slits between the grains. This phenomenon is connected with the release of water molecules hydrating silver cations, what causes that Keggin ions come closer to each other. These results are concurrent with the results obtained with XPS technique for used

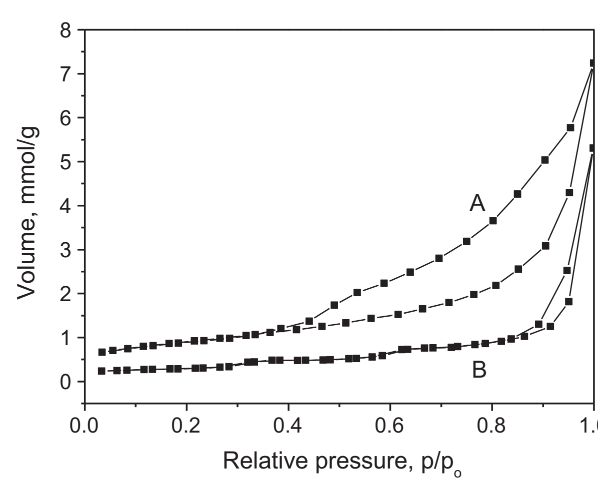

Fig. 10. The adsorption–desorption isotherms of the used catalyst after dehydration reaction performed in air-10% (A) and air-2% (B).

catalysts [26] which exhibited the changes in the surface composition of AgPW after reaction in air-2%. It can be concluded that hydrothermal stability of AgPW catalyst in dehydration of ethanol greatly depend on relative humidity of atmosphere in which reaction is performed. This indicates that the application of bio-ethanol, which contains some amount of water, can facilitate the performance of catalyst.

Taking into account the results concerning conversion of ethanol and selectivity to ethylene it can be concluded that the AgPW salt is a potential catalyst for the production of ethylene from ethanol. This reaction can be performed even in air atmosphere at relatively low temperature with very low quantity of side products. It is important to underline that oxygen did not inhibit the reaction. It can be suggested that the temperature range of reaction (373–493 K) was too low to oxidize the ethanol. On the other hand, it is supposed that the dehydration of ethanol-water mixture, e.g. bio-ethanol performed in air atmosphere can be low cost-effective process in the future.

The presented results are very important from environmental point of view showing that it is possible to produce ethylene from ethanol even in air atmosphere and at relatively low temperature with very high conversion and selectivity. Thus, the neutral silver salt AgPW can be recognized as a stable 'ecofriendly' catalyst.

4. Conclusions

The neutral silver salt of tungstophosphoric acid $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ forms two different secondary structures depending on temperature and relative humidity of atmosphere. The first one contains one water molecule bonded to each silver cation while the other is formed after its loss. The XRD measurements showed that the loss of water coordinating silver cations proceeds in the temperature range of 473–523 K. However, lower relative humidity of atmosphere can significantly decrease this temperature.

The $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt was investigated in nitrogen and air atmosphere with different relative humidity as the catalyst in dehydration of ethanol. The conversion of ethanol performed in atmosphere with relative humidity equal to 10% substantially exceeded that obtained in atmosphere with lower relative humidity equal to 2%. It can be suggested that 10% of relative humidity of atmosphere, which was a carrier gas for ethanol, stabilizes the hydrated form of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt in temperature range of 373–493 K. The presence of oxygen did not influence the oxidation process of ethanol as well as did not inhibit reaction, probably as a result of low temperature reaction. The stability of $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt after reaction was studied using FT-IR and XRD methods. It was shown that $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt is stable in the reaction conditions or easy restores its structure in atmosphere with higher relative humidity. This is important because the water molecules hydrated silver cations are necessary to generate protons needed to acidic type reaction.

Thus, it can be concluded that $Ag_3PW_{12}O_{40}{\cdot}3H_2O$ salt is promising material for the preparation of 'ecofriendly' and industrially applicable catalyst for ethylene production by dehydration of ethanol even in air atmosphere in relatively low temperature. On the other hand, the use of ethanol with some amount of water like bio-ethanol can be important from environmental and economic point of view.

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